areas were temporarily deposited in these sections. The sections were marked and separated from each other in order to ensure the necessary handling area and technique (cultivators, cisterns, lorries). Soil of approximately the same contamination characteristics and content was placed in every sector. The objective of this set-up was to achieve the most effective process of *ex-situ* remediation in the sense of process optimisation (e.g. the retention time). The excavated soil was distributed on the site so its full aeration was ensured (average soil height was 90 cm). After verification of the achieved TPH limit (control sampling was done by the supervising organization, Fig. 2) the decontaminated material was sequentially transported back into excavated areas for backfilling.

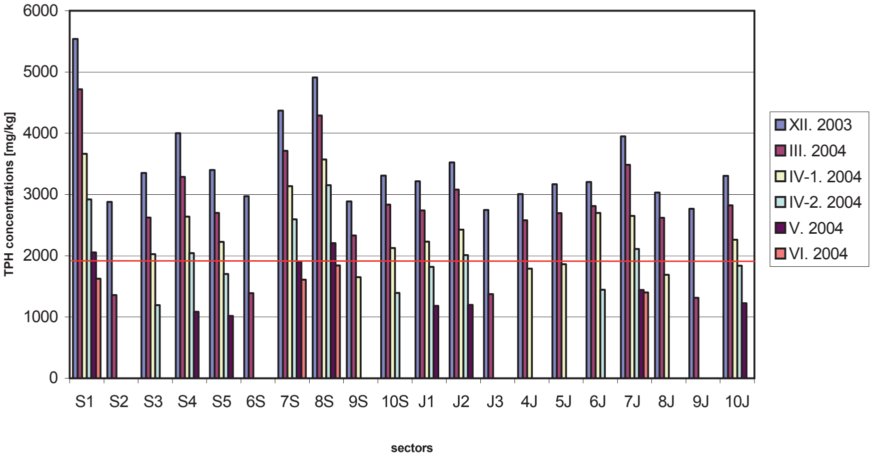

Figure 2. Soil TPH concentration during ex-situ biodegradation

The principle of biodegradation method is based on the ability of certain bacterial strains to utilize the existing contaminant (in the case of Zatec airport it is jet fuel – kerosene) as carbon and energy source in oxidation processes. Environmentally undesirable hydrocarbons (in case of kerosene, they are mainly aliphatic alkanes – linear and also branched, cycloalkanes, aromatic hydrocarbons and alkylated aromatic hydrocarbons) are decomposed following a standard metabolic pathways, through several intermediate stages, to carbon dioxide and water. Soil cultivation (loosening) was performed twice in the total volume of the treated soil during biodegradation process. Soil cultivation was carried out due to three following reasons: material aeration, uniform distribution of biopreparation and/or additives and material homogenisation. Cultivation was firstly performed by re-ploughing and soil shifting by scoop-loaders, in the second stage.

After finishing the excavation work, the bottom of remedial excavations was made into downhill grade, in direction of the underground water flow, and loosened to ensure an infiltration area for the applied biopreparation solution and mineral enrichment. Drainage distribution systems were installed on prepared bottom. At the same time, a central delivery system of the biopreparation solution, drawn from a technological centre to individual remedial excavation areas, was laid down. Infiltration drains were backfilled (recycled concrete, 10 mm grain size) up to 0.5 m thickness.

After performing the preliminary *in-situ* remedial work, the excavated zones were backfilled with decontaminated soil from the biodegradation field. Backfilling was performed building 0.5 m – thick – layers, which were compacted by a vibrating roller. This work was finished in December 2004.

During *ex-situ* remedial work 118,382 m^3 of contaminated soil were excavated, decontaminated and backfilled. Necessary inert materials (with contaminant content below the limit) were excavated in volume of 64,612 m^3. Within the framework of preliminary work (carried out before the beginning of the own *ex-situ* remediation) 374 m of steam piping and 2,909 m of sewerage were eliminated,, together with reprocessing of 14,673 t of wrecking rubble and 3,344 t of concrete resulting from the demolition work. At the same time other systems i.e. water piping, heavy- and light-electric power cables were also removed.

Within the soil decontamination work of the former runway 3,474 m^3 bacterial preparation, 421 m^3 liquid fertilizers and other additives were applied. During the remedial work monitoring and management systematic samples were collected and analysed: 4,877 soil samples and 283 underground water for determination of petroleum substances, 1,137 soil samples for biodegradation parameters and 471 samples of bacterial preparations for microbial quality.

Summing up, a total of 411.4 t of petroleum substances were removed during the *ex-situ* soil remediation.

4.2. IN-SITU SOIL REMEDIATION

The preliminary work of *in-situ* remediation consisted on laying down a 1,842 m delivery system for biopreparation distribution and 1,956 m of infiltration drains. 29 hydrogeological monitoring wells and 30 large-dimension remedial wells were further built. 119 ground water samples from the former as well as the newly constructed monitoring wells were drawned and analysed.

The monitored parameters, for this paret of work, were the followings: total petroleum hydrocarbons (TPH), content of dissolved oxygen, redox potential, temperature, conductivity and pH of water, content of nitrates and phosphates, data on chemical and biological oxidation demands in water samples and final bacterial activity. The obtained results were used within the optimisation of the applied biodegradation method.

Figure 3. Biodegradation technological centre

Before starting the *in-situ* biodegradation work the application of fertilizer solution (called "mineral enrichment") was necessary. As result, the maximal intensification of the naturally occurring microflora activity was achieved. The intensification results of the controlled dosage of mineral nutrients and micro-elements necessary for degradation activity performed by autochthonous; optionally introduced microorganisms. The composition of the applied fertilizer solution allows continuation of microbial metabolisms in anoxic conditions, in the case of limitation of air oxygen, in low permeable parts of the underground body. The solution is prepared in the biocentre (Fig. 3), in retention tanks, by diluting the liquid fertilizer with pre-treated ground water (taken from the well system of the hydraulic barrier). Mixing ensures complete dispersion of contingent sediment. Afterwards, the solution is delivered via pumping through the pipeline system into the infiltration drains, to the appropriate remedial excavations.

The *in-situ* method, as such, solves problems of re-treatment of the saturated zone contaminated with biologically treatable contaminants. It directly comes from the *pump&treat* technology and integrates biological elements into this classical technology. The method principle is based on optimisation of biodegradation process conditions, mainly in saturated zone of an underground environment. It uses natural biodegradation activity of autochthonous microflora as well as directly isolated bacterial strains, which are delivered into the underground environment. Aeration of pumped water and its enrichment with deficient nutrients (mainly nitrogen and phosphorus) and/or other way of electron acceptor dosage are applied for their activity stimulation.

Regular application of bacterial preparation started in November 2004 and it has been carried out, via infiltration drains, since then.

The *in-situ* remediation work will still continue up to the end of 2008 and, periodically, the quality of ground water will be observed up to 2013, within a post-remedial monitoring process in the whole premises.

4.3. PROTECTIVE REMEDIAL PUMPING AND UNDERGROUND WATER

Groundwater has been pumped from all 30 hydrogeological wells, which are forming the outside hydraulic barrier. The extracted groundwater is being treated in three containerized wastewater treatment stations. Both free phase of petroleum substances and dissolved organic contaminants are removed in these stations.

The remedial facility (station) is standardised and each consists of the following parts: a retention tank of pumped treated water with a support, a gravitation-coalescence separator, a labyrinth adsorption tank, a discharging pump, automatic control and electrical equipment, connecting pipeline, pipe fittings and water meters.

The treated ground water is used for production and dilution of bacterial preparation utilised within the remediation process. The *in-situ* technology is then a closed cycle of derground water: pump – treat – back infiltration. Due to this method, flushing of contaminated soils in the saturated zone is accelerated. The *in-situ* remediation has minimal demands terms of space requirement and thus it enables construction of communications, engineering systems and other equipment on the premises.

Within the remedial pumping process, approx. 46,000 m^3 of contaminated ground water is annually pumped and further treated from the hydraulic barrier wells.

5. Conclusions

The presented remediation case studyof the Zatec military airport is one of the largest remedial actions in Central and Eastern Europe.

During airport operation petroleum hydrocarbon substances stored and used on its premises caused massive pollution of 120,000 m^3 of unsaturated zone and 100,000 m^3 of saturated zone.

Systematic remedial activities of the site started with additional remedial investigation in August 2003. It was further followed by *ex-situ* biological remediation of the unsaturated zone, which was successfully finished in June 2004. During this phase 118,382 m^3 of soil contaminated above the target limit were excavated,, biologically decontaminated and backfilled. 411.4 tons of petroleum substances were removed.within the process.

At the moment, the saturated zone *in-situ* bioremediation is being carried out. This part of remediation work should proceed up to the end of 2008 and post-remedial monitoring is planned up to 2013.

AQUIFER REMEDIATION AND CHEMICAL RECOVERY FOLLOWING A SPILL DUE TO AN EARTHQUAKE IN TURKEY

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Abstract. In the aftermath of the August 1999 earthquake in Turkey, ruptures in piping connections of storage tanks resulted in an acrylonitrile spill. A post-incident risk assessment revealed that the acrylonitrile concentrations in the seawater and sediments rapidly decreased down to non-detect levels within a month of the incident. Periodic monitoring data revealed that the acrylonitrile contamination was limited to on-site soil and shallow groundwater at the site. A shallow groundwater monitoring and extraction program was initiated in October 1999. Groundwater had been pumped out of 3 manholes and 4 drainage ditches installed on-site. Acrylonitrile concentrations in one of the monitoring wells decreased from an initial high of 80,000 ppm down to non-detect levels at the end of the third year. This paper presents the hydrogeological setting, chemical recovery efficiency and successful outcome of a long-term environmental project on groundwater quality monitoring and shallow aquifer remediation following a chemical spill.

Keywords: chemical spill, aquifer remediation, groundwater extraction, chemical recovery

1. Introduction

The acrylic fiber manufacturing facility is located on the southern coast of the Marmara Sea, approx. 20 km. west of city of Yalova, Turkey (Figure 1). The facility has been in operation since early 1970s. Bulk chemicals are stored in a tank farm located on the coastline.

In the aftermath of the 17 August 1999 earthquake, three of the six on-site storage tanks were damaged at an acrylic fiber manufacturing facility and approximately 6,500 tons of acrylonitrile (ACN) was released into the environmental media due to ruptures in piping connections. No fire and fatal injury

M.D. Annable et al. (eds.), Methods and Techniques for Cleaning-up Contaminated Sites, 91–101.

occurred at the incident, which was directly attributed to the company's effective implementation of the Responsible Care® initiative of the world chemical industry, which was acknowledged in an ICCA-UNEP report submitted to the World Summit on Sustainable Development in Rio de Janeiro (2002a).

Majority of the spilled ACN liquid was released into the sea, whereas the rest seeped into the soil and vaporized. ACN, a chemical of high volatility potential at ambient conditions, readily biodegrades in the environmental media when diluted. A risk assessment conducted by the Turkish government agencies and research institutions revealed that the ACN concentrations in the sea water and shallow sediments rapidly decreased down to non-detect levels within a month of the incident, and the surface water sources, the vegetables and fruits in the nearby fields were not impacted. Cyanogenic impact of the chemical vapors was limited to a 200-meter radius of the tank area, as observed on browning of leaves of the shrubbery on-site (2001). There has not been reported a negative impact of the incident on human health to date.

Figure 1. Facility Location

2. Remedial Investigation Program

The facility is located on relatively compacted lower segment of a Pliosen age alluvial fan. Based on the available geotechnical borehole information, the tank farm area consists of a 4-6 meter-thick compacted fill and silty/sandy layer underlain by a min. 5 meter thick plastic clay layer overlain an another silty/sandy material layer throughout the length of 20 meter borehole logs.

The facility management initiated a long-term environmental investigation program immediately after the incident in coordination with the Turkish Ministry of Environment. The objective of the investigation was to determine the nature and extent of potential contamination in the sea, surface water and ground water and the surface soil and sediment quality.

The subsoil investigations in the vicinity of the tank farm revealed that the extent of soil contamination was vertically contained within the surficial 1 to 2 meter-thick compacted fill material.

Presence of the consolidated clay layer provided an aquitard barring the contaminated groundwater migration to the deeper aquifer as demonstrated by the absence of any ACN in the water samples collected from the facility's deep production wells. Lateral extent of this shallow groundwater contamination was also limited to facility boundaries due to presence of two water channels on the site boundaries providing natural hydrogeological barriers. A conceptual hydrogeological setting of the tank farm area is presented on a block diagram in Figure 2.

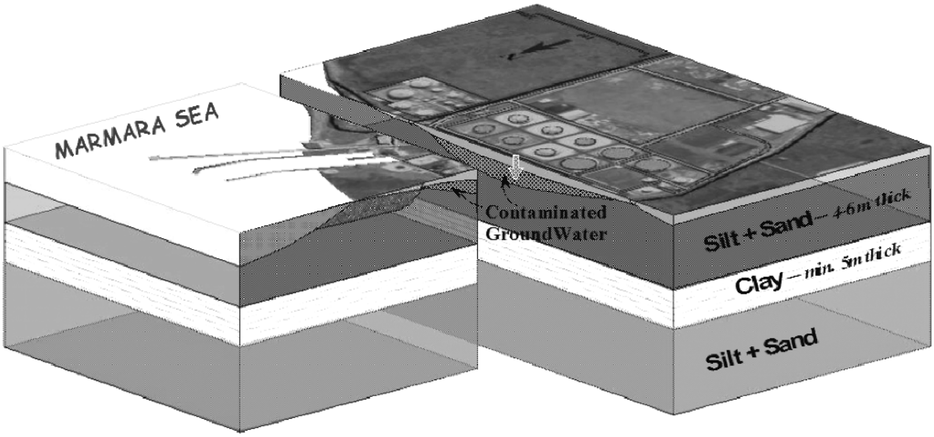


Figure 2. Conceptual hydrogelogical setting of the site

A shallow groundwater quality monitoring and extraction program was initiated in October 1999. Groundwater was monitored at 24 locations and pumped out of 4 installed drainage ditches *(french drains)* and 3 manholes installed on-site. The extracted groundwater was treated for acrylonitrile recovery at the facility's solvent distillation unit and then sent to the facility's wastewater treatment plant.

2.1. GROUNDWATER MONITORING PROGRAM

Shallow groundwater quality had been monitored for ACN, pH, temperature and specific conductivity parameters at 24 monitoring locations for seven years, between September 1999 and September 2006. Sampling frequency was bi-weekly for two months, weekly for 3 years, bimonthly for 2 years and monthly for the last two years. Groundwater monitoring locations are presented in Figure 3.

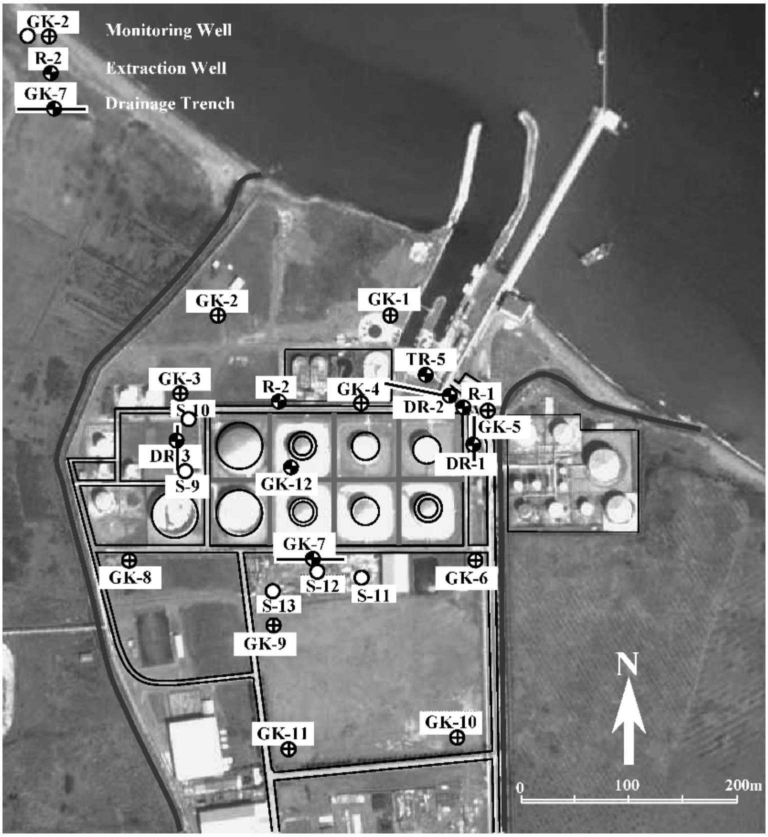


Figure 3. Groundwater quality monitoring and drainage trench and extraction well locations

Soil and groundwater sampling results at several offsite locations in the vicinity of the tank farm area revealed that the ACN contamination was limited only to on-site soil and shallow ground water in the vicinity of the tank farm area. No residual surface and sea sediment contamination was detected.

At the onset of the project, 11 monitoring wells (15 cm diameter steel casing) were installed (GK-series). Additionally, 5 existing geotechnical borings were converted to uncased monitoring wells by plugging the bottoms in the clay layer (S-series).

In the first month, three existing sumps located downgradient of the tank farm (R1, R2 and TR5) were used as the extraction points for groundwater. At the end of the first month of the project, one standalone extraction well (GK-12) and three drainage trenches (DR-1, 2 and 3) and GK-7 monitoring well were also converted to a drainage trench to expedite extraction efficiency. Typical construction details of the extraction wells are presented in Figure 4 (a) and (b).

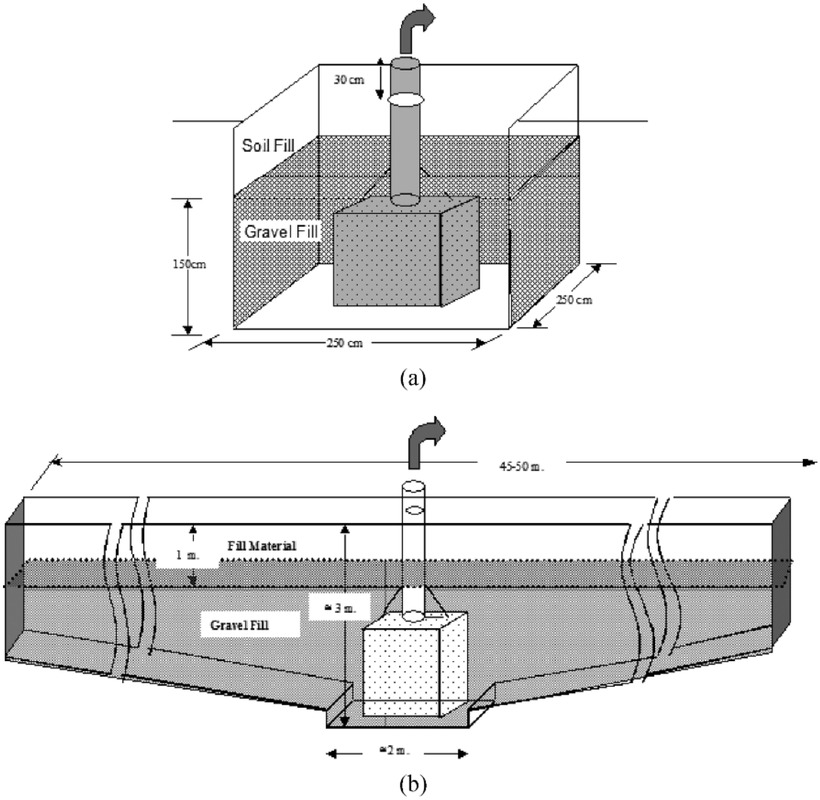


Figure 4. Typical details of (a) extraction well point and (b) drainage trenches (french drain)

2.2. GROUNDWATER EXTRACTION AND TREATMENT

Submerged pumps with level-switches were installed at each extraction point. Extraction of contaminated groundwater started at three facility drainage sumps located downgradient of the spill area at a total daily average of 35 m^3. This quantity was increased to an average 80 m^3/day after installation of the other drainage trenches. Extracted groundwater was sent to a 5,000-ton storage tank via pipeline.

Collected contaminated groundwater was sent to a dedicated distillation unit at the plant for recovery. At the end of the first year of operation, the acrylonitrile concentrations in the extracted water decreased significantly below recovery efficiency level of the distillation unit. Thence, the extracted water was diverted to the facility's wastewater treatment unit until the end of the extraction program. Groundwater extraction and treatment operation continued for 4 years, until the end of 2004. A total of 53,000 m^3 of groundwater was extracted and treated. The quantity of pumped and treated groundwater is presented in Figure 5.

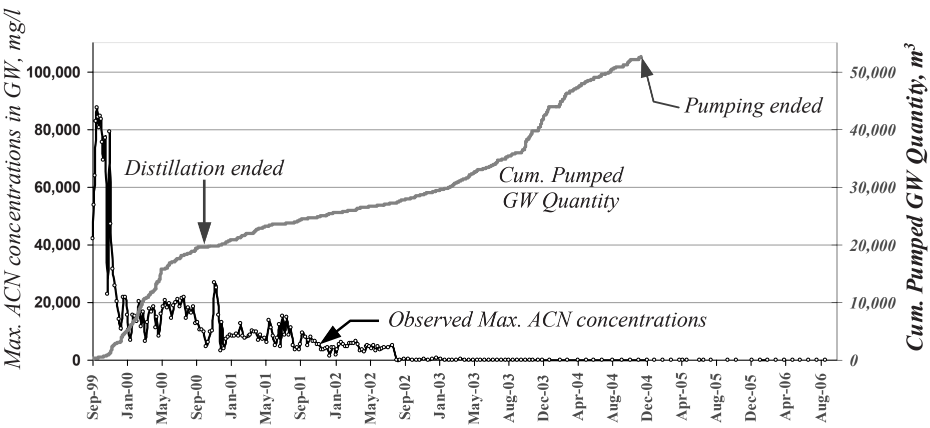
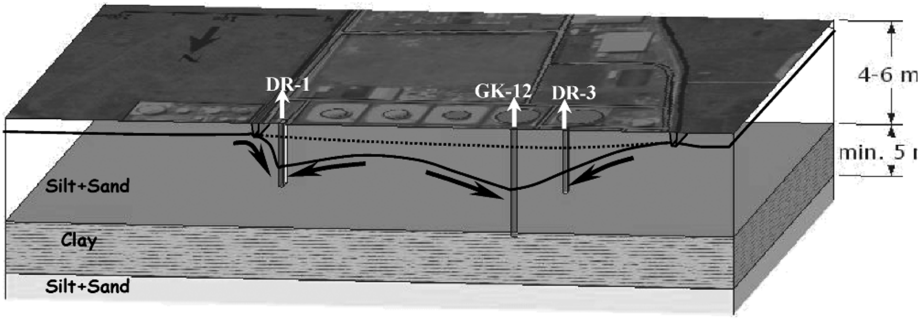


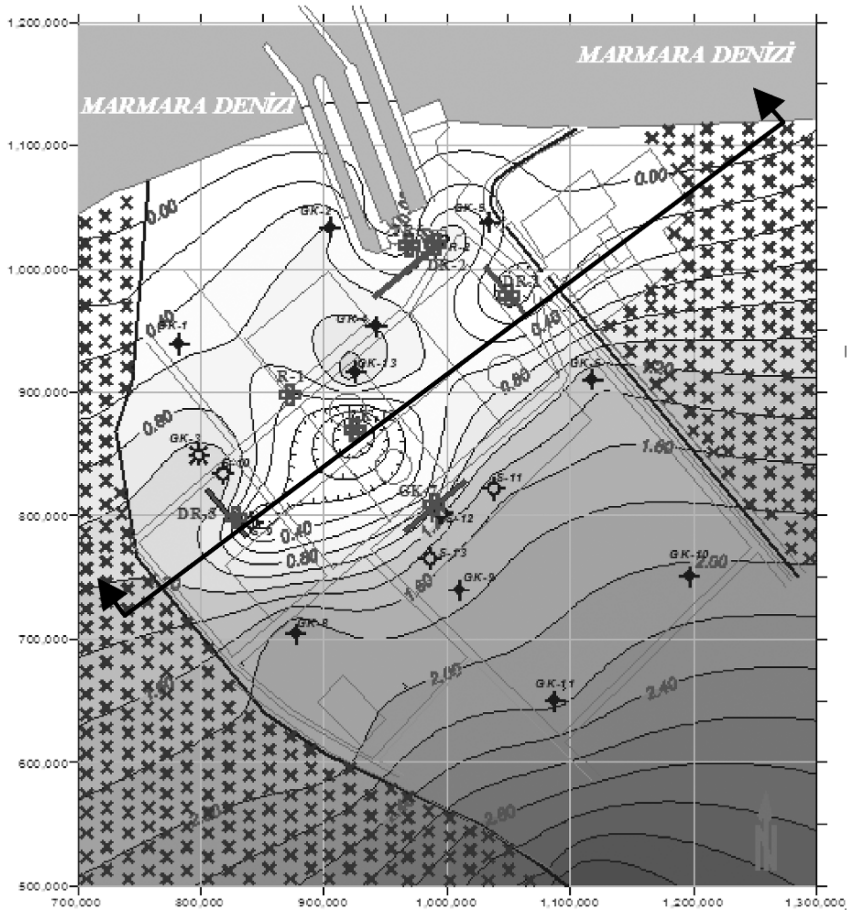
Figure 5. Pumped and treated groundwater (GW) quantities and ACN concentrations

2.3. ON-SITE CONTAINMENT OF CONTAMINATED GROUNDWATER

The continuous groundwater extraction at the wells and drainage trenches further enhanced the natural onsite containment of the contaminated groundwater by lowering the water levels underneath the tank farm area as shown in the schematic block diagram and a recorded groundwater level graph are presented in Figure 6 (a) and (b).



(a)



(b)

Figure 6. On-site containment of groundwater (a) and the representative piezometric levels (b)

2.4. GROUNDWATER QUALITY MONITORING RESULTS

During this seven year long project, 243 rounds of groundwater samples, collected from 24 locations, were analyzed for acrylonitrile. Piezeometric level and ACN distribution maps for each sampling round were used in optimization of the groundwater extraction efficiency for removal of the residual contamination in the aquifer. A sample of the ACN distribution map and relevant recorded parameters are presented in Figure 7.

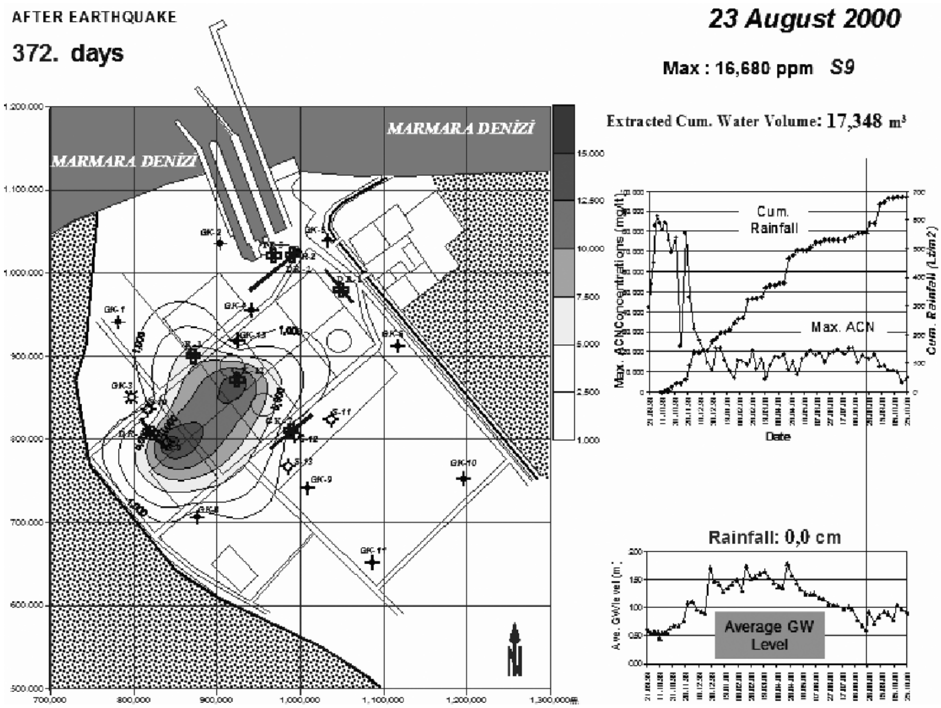


Figure 7. Graphical records of ACN distribution, rainfall and pumping data for 23 August, 2000

3. Contaminant Removal - Model

At the onset of the groundwater extraction activities, the following symptomatic relationship between the piezometric level, ACN concentrations and rainfall was observed at the extraction wells:

- The ACN concentrations at the extraction well points showed a systematic variation following restart of pumping after pump malfunctions. Such observations were tracked and it was concluded that the ACN concentrations showed an increasing trend as the piezometric levels at the extraction wells were lowered during the groundwater extraction. As pumping was halted for a couple of days, the ACN concentrations decreased.

- ACN concentrations showed a general decreasing trend as the piemetric levels in all monitoring locations rose after intermittent rainfall events.

ACN is a highly polar organic chemical and has a "very low to negligable" adsorbtion potential to clay and other minerals in soils. The observations above led us to a hypothesis that ACN present in the unsaturated soil between the surface and the water table was scrubbed into the shallow aquifer by the percolating rainfall and then effectively dragged into the extraction well by the increased hydraulic gradient of the extraction well drawdown cone. This concept was applied to the groundwater extraction scheme with the programmed halt-and-go schedules in order to optimise the ACN extraction efficiency.

A seven-year record of maximum ACN concentrations, average groundwater level, annual cumulative rainfall and cumulative groundwater extraction volume are presented in Figure 8.

A conceptual model for the experimentally-verified soil washing/water extraction process is presented in Figure 9.

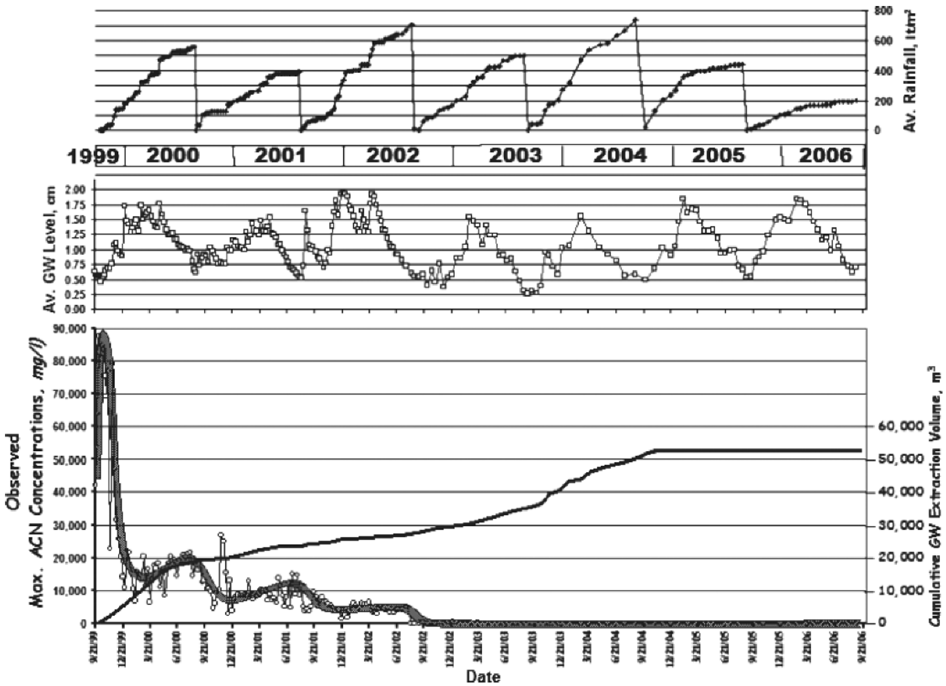


Figure 8. Seven-year record of the maximum ACN concentrations, average groundwater level, annual cumulative rainfall and cumulative groundwater extraction volume

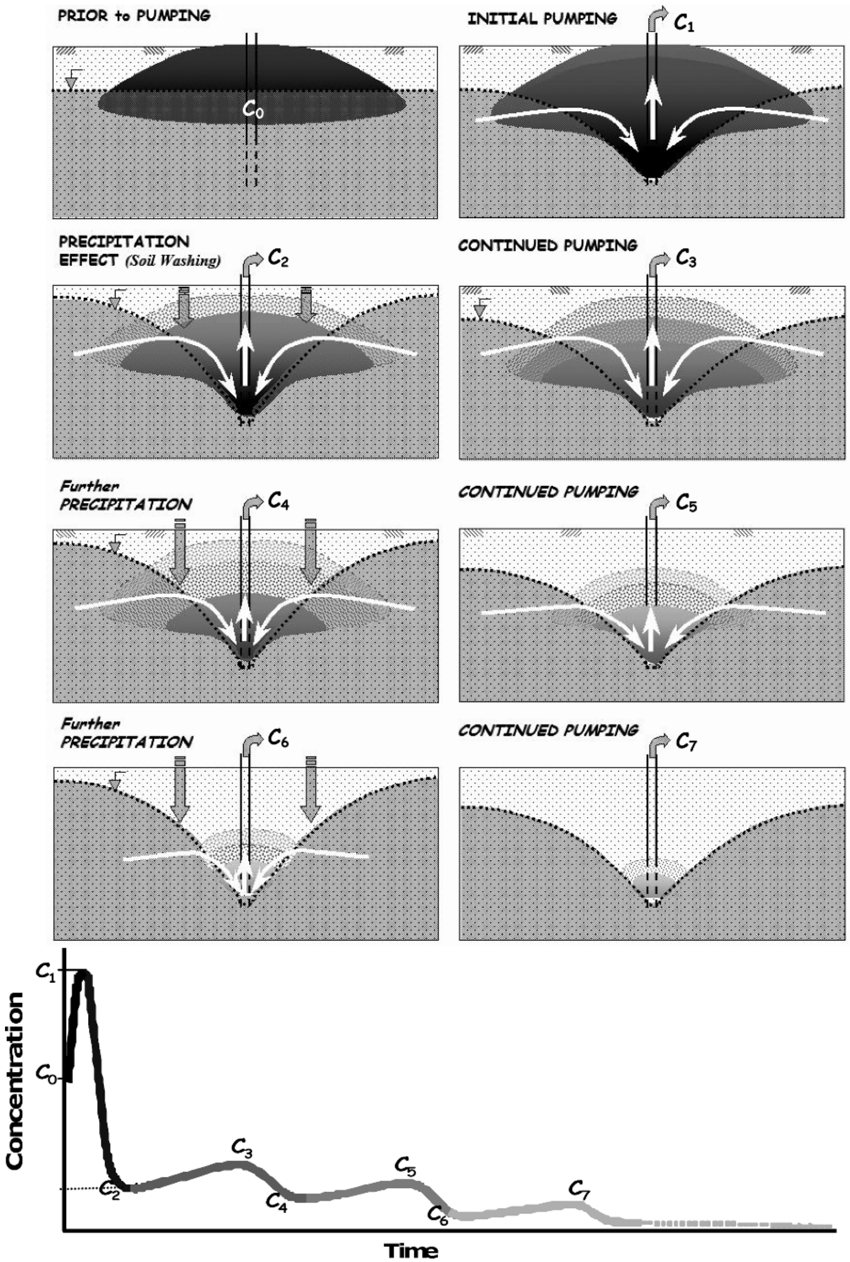


Figure 9. Conceptual model for spilled chemical removal via groundwater extraction from granular non-adsorbing medium

4. Conclusions

Earthquakes are natural events that have been causing disaster level disruptions in all aspects of human life. Disaster preparedness is a key factor in minimizing the impacts of such events on the communities. The case history presented in this paper reveals that fatalities and fires at major industrial facilities can be prevented with properly taken process safety measures, even under the worst post-disaster circumstances and major chemical spills can be remediated effectively.

The case history presented in this paper reveals also that a good understanding of the local geology, hyrogeological setting and implementation of an effective pump/treat scheme, optimized with continuous monitoring of some basic parameters (water quality, piezometric levels and precipitation) play a key role in the success of on-site containment of chemical spills and remediation of shallow aquifers.

Acknowledgement

The author extends his sincere thanks to the management of the AKSA Akrilik Kimya AS of Turkey for their conscientious efforts for immediate initiation of the groundwater quality monitoring and remediation program. Special appreciation is also extended to the memory of late Mr. S. Ergin and to Mr. M. Yilmaz, past and current general managers of the company for their dedication to this rigorous monitoring and extraction efforts that continued for seven years. Special appreciation goes to the Turkish Chemical Manufacturers Association for its continued technical support for the project under the Responsible Care® initiative of the world chemical industry. This paper was presented at the NATO Advanced Research Workshop in Sinaia, Romania on 10 October 2006 as an invited lecture.

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